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Raman Spectra of some Organic Crystals and Solutions

By

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(Received for publication, 18th August, 1931)

Abstract.

Raman spectra of a number of crystalline acetates, oxalic acid, ammonium oxalate, hexachlorethane, urea and hexamethylene tetramine have been studied. The changes in the frequencies when dissolved in water have been examined with lead acetate, urea and hexamine. Striking changes in the C—H frequencies are observed in the case of hexamine when passing into solution, probably due to the formation of a hydrate. Practically no changes take place when hexachlorethane is dissolved in CCl_4 or ether.

The C=O frequency (usually about 1700 cm^{-1}) fails to appear in the spectra of the acetates and of urea, though they are supposed to contain the C=O linkage. The possibility of urea existing in a tautomeric form not containing the carbonyl group is discussed.

Introduction.

In the previous investigations,[1] the substances examined by the author in the form of crystal powder were mostly inorganic, though consisting of fairly simple molecules. An attempt has now been made to extend this method to simple organic substances of the aliphatic group. The transmission method was employed as described in a previous paper. The light from two pyrex mercury arc lamps was passed through

[1] Krishnamurti, Ind. J. Phys., 5, 1, 105, 113, 183, 587, 633, 651 (1930); 6, 7 (1931)

a suitable thickness of the powder, and the transmitted light focussed on the slit of a high dispersion Fuess glass spectrograph. Various filters were interposed between the light source and the substance wherever necessary :— (1) A concentrated solution of didymium nitrate of about 1 cm. thickness, to diminish the continuous spectrum of the mercury arc in the immediate neighbourhood of the 4358 line; (2) A dilute solution of uranin to transmit the 4046 group of lines freely and clear the region beyond λ4600A; (3) A dilute solution of the sodium salt of o-cresolphthalein to transmit only the 4358 group of lines, and to diminish the continuous spectrum after λ4600A. The last filter was found to be extremely useful, has been used extensively by the author both for the investigation of crystal powders and of liquids. An iron arc comparison spectrum was taken on each plate for accurate measurement of the lines.

Results.

Acetates :—Ammonium, cadmium, zinc and lead acetates were examined, as well as a concentrated aqueous solution of lead acetate. The results for these as well as for pure acetic acid are given in Table I. It will be seen that two lines come out prominently, one at 956 cm^{-1} and the other at 2937 cm^{-1}. The corresponding lines in acetic acid (889 and 2940 cm^{-1}) are also very strong. Two of the weaker lines of acetic acid also appear in lead acetate crystals as rather sharp lines. But, curiously enough, the 1670 cm^{-1} frequency of acetic acid, attributed to the C=O bond, does not appear in any of the acetates. This has already been remarked by Ghosh and Kar,[2] who think that whenever the C=O group forms part of a negative ion, it gets weakened considerably.

[2] Ghosh and Kar, J. Phys. Chem., *35*, 1735 (1931)

The frequency at 2937 cm^{-1} could be attributed to the C—H oscillation of the CH_3 group, and it does not show any variation with the different acetates or acetic acid. The other one at about 950 cm^{-1}, however, which could be attributed to the C—C bond, though practically in the same position for the less electropositive cations, shows a smaller shift for ammonium acetate, approaching the value for acetic acid. A very slight shift in the same direction (9 cm^{-1}) is observed in the case of lead acetate in a concentrated aqueous solution, where all the lines get broadened also.

TABLE I

Exciting line, 4358·3A (22938 cm^{-1})

Substance	W. l. of Raman line in I. A.	Wave no ν	$\Delta\nu$	Intensity	Remarks
Lead Acetate cryst.	4546	21991	947	Weak	
	4592	21771	2934	Medium	4046 excitation
	4631	21588	1350	V. weak	
	4648	21509	1429	,,	
Lead Acetate. Aqueous Soln.	4544·1	22000	938	Strong	
	4592·7	21768	2937	,,	4046 excitation
	4631	21588	1350	Weak	
	4648	21509	1429	,,	
Cadmium and Zinc Acetates.	4547·8	21982	956	Weak	
	4592·6	21768	2937	Medium	4046 excitation
Ammonium Acetate	4542	22011	927	Weak	
	4592,6	21768	2937	Medium	4046 excitation

* Acetic Acid : $\Delta\nu$=440, 614, 889, 1280, 1368, 1432, 1669, 2940

* Amm. Acetate Soln. : $\Delta\nu$=653, 923, 1346, 1410, 1756, 2927

(Values given by Dadieu and Kohlrausch.)

Oxalic acid and Ammonium Oxalate :—Oxalic acid crystals $(COOH)_2$, $2H_2O$ gave only one frequency at 855 cm^{-1}. This probably represents the symmetrical C–C oscillation. In ammonium oxalate, however, even this frequency was not observed, but only one at 3215 cm^{-1}, which is probably the symmetrical oscillation of the NH_4 group, and corresponds to one of the frequencies in ammonia. As the results were not very encouraging, other oxalates were not examined.

Hexachlorethane :—Kahlbaum's preparation was recrystallised from alcohol, and examined by the transmission method. Three distinct lines were observed, the first two very sharp and the third slightly diffuse. The values showed a good agreement with those observed in a solution [3] of CCl_4 or of ether, [4] due to the non-polar character of the constituents.

Urea :—Merck's extra pure preparation was used. It gave a strong line at 1006 cm^{-1}, and a very faint one 1150 cm^{-1}. The strong line was shifted to 999 cm^{-1} in a concentrated aqueous solution. Two more frequencies, 513 and 578 cm^{-1} were seen faintly in the spectra of the solutions, and intensified on the addition of hydrochloric acid. There was, in addition, a broad band at about 3μ.

Hexamine :—This interesting substance has been fully analysed by means of X-rays, and the positions of the atoms in the molecule have been determined. As it crystallises in the cubic system, and at the same time is very soluble in water, the Raman spectra of the crystals and of the solution were compared. The essential difference between the two spectra was in the frequencies attributable to the C–H aliphatic bond. In the crystals, they consisted of a sharp line (2953 cm^{-1}) with a very weak component to the left, whereas in a concentrated solution the strong line had shifted considerably (2977 cm^{-1}) and broadened while the faint component became much more intense.

[3] Bhagavantam and Venkateswaran, Proc. Roy. Soc., A *127*, 365 (1930)
[4] Dadieu and Kohlrausch, Monatsh, *55*, 58 (1930)

Hexamine is formed by the simple addition of formaldehyde and ammonia :

$$6CH_2O + 4NH_3 \longrightarrow C_6H_{12}N_4 + 6H_2O$$

A mixture of formaldehyde (40% formalin solution) and ammonia in the right proportions gave the same Raman spectrum as that of the hexamine solution. There was a difference in the relative intensities of the lines, however, when the proportion either of formaldehyde or of ammonia was in excess. Incidentally, the Raman spectra of formalin as well as of ammonia solution (25%) were taken. The results are tabulated below :

TABLE II

Exciting line, 4358·3A (22938 cm^{-1})

Substance	W. l. of Raman line in I. A.	Wave no. ν	$\Delta\nu$	Intensity
Oxalic acid cryst.	4527	22083	855	Weak
Amm. Oxalate	4652	21490	3215	Med.
Hexachlorethane.* C_2Cl_6	4424·2	22597	341	Med.
	4442·3	22505	433	Str.
	4490	22265	673	V. weak
	4527	22083	855	weak
Urea cryst.	4558·2	21932	1006	Str.
	4585	21804	1134	V. weak
Urea soln.	4462	22405	533	V. weak
	4556·8	21939	999	V. str.
	4590	21780	1158	Weak, diff.

* In CCl_4 : 345 (0) ; 434 (2) ; 860 (1).....B & V.
In ether : 145 ; 214 (2) ; 340 (2) ; 431 (3 br.) } D & K.
In alcohol : 146 ; 219 (2) ; 337 (2) ; 423 (2) }

TABLE III

Exciting line, 4358·3A (22938 cm^{-1})

Substance	W. l. of Raman line in I.A.	Wave no. ν	$\Delta\nu$	Intensity	Remarks
Formalin soln.* about 40%	4538	22030	908	Med.	
	4561	21919	1019	V. weak	
	4579	21833	2872	Weak br.	4046 excitation
	4587	21795	2910	Med.	Very broad
	4605	21709	2996	,,	4046 excitation
	4661	21449	1489	Med. br.	
	4272	23402	1303	V. weak	4046 excitation
Ammonia soln. (25%)	4673	21394	3311	Str. br.	4046 excitation
	4691	21311	3394	Weak	,, ,,
Hexamine cryst.	4511·5	22159	779	Med.	
	4568·5	21883	1055	Str.	
	4593	21766	2939	V. weak	4046 excitation
	4596·1	21752	2953	Str.	
	4631·5	21585	1353	V. weak	
	4654	21481	1457	Weak	
Hexamine soln.	4446·7	22481	457	Med.	
	4458	22425	513	Weak	
	4512·1	22156	782	Str.	
	4520	22118	820	V. weak	
	4558·7	21930	1008	Med.	
	4567·8	21886	1052	Med.	
	4630·1	21592	1346	,,	
	4653	21486	1452	,, diff.	
	4595	21757	2948	Str.	4046 excitation
	4601	21728	2977	Str. br.	,, ,,

* Values given by Hibben for formalin solution are :

$\Delta\nu$ = 802, 909, 1055, 1285, 1479, 2840, 2915, 3015, 3087.

Discussion of Results.

Acetates :—The maximum number of lines has been obtained only with lead acetate crystals. The agreement between the values for all the acetates is evident, and only small changes accompany their passage into solution. The frequency attributable to the C−C bond is the only one which shows any change, and even this change is observed with strongly positive cations; the direction of the change is towards the value for acetic acid.

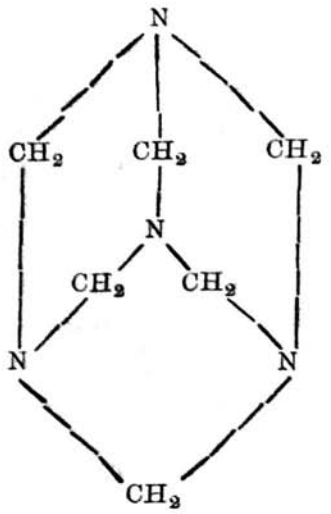
Urea :—The strong line in urea at about 1000 cm^{-1} could be attributed to the C−N bond, as in the simple aliphatic amines. This changes only by a few wave-numbers on passing into solution. According to the formula usually attributed to urea, $O=C\langle^{NH_2}_{NH_2}$ which is supported also by X-ray evidence, the C=O bond is present, but it is very surprising that the frequency at about 1700 cm^{-1} usually attributed to it does not appear in the spectrum of the crystals or that of the solution. An additional frequency (about 600 cm^{-1}) which is also attributed to the same bond appears faintly in the spectrum of urea solution. It is quite possible, therefore, that the tautomeric form is also present, and that one H atom in NH_2 might be oscillating between the O and N atoms thus :

$$O=C\langle^{NH_2}_{NH_2} \rightleftharpoons OH-C\langle^{NH_2}_{NH}$$

The second formula is sometimes attributed to urea since it reacts only as a mono-acid base. This shifting of the hydrogen atom cannot be perceived in X-ray analysis as the scattering by the H atom is negligible. Pal and Sengupta[5] have reported a line at 830 cm^{-1} which could not, however, be observed by the author.

[5] Pal and Sengupta, Ind. J. Phys., 5, 24 (1930)

Hexamine:—The molecule of hexamine is usually represented as follows :



It will be seen that the most prominent lines would be due to the C−N and C−H bonds, and actually the strongest lines in the crystal are 780 cm^{-1} and 2955 cm^{-1}. Though the C−N frequency in urea is about 1000 cm^{-1}, the closed nature of the chain in hexamine is probably responsible for its low value. The changes observed in the C−H frequencies in solution, *viz.*, the brightening up of the faint line and displacement of the stronger line, are no doubt connected with the power of hexamine to form a hydrate, $C_6H_{12}N_4$, $6H_2O$, m.p. 15°C. It is likely that the water molecule is situated in the neighbourhood of each carbon atom, and hence influences the C−H frequencies. The aqueous solution of hexamine is feebly basic, and it is also able to form a stable dibromide. Further, there is considerable evolution of heat when the crystals are dissolved in water. All these facts show that the frequencies of the molecule should be modified in solution, and the Raman spectra show that the change is essentially connected with the C−H oscillation.

Formaldehyde:—This has recently been investigated by a number of workers in aqueous solution.[6] It shows several frequencies most of which are very broad and diffuse. The number of frequencies present show that it is not a simple molecule in solution; and as molecular weight determinations show[7] it is probably $(CH_2O)_3$, H_2O. The essential feature here is that the C—H frequencies are just resolved into two broad bands the region between them being quite dark. In the same region, hexamine shows two lines as mentioned previously. Ammonia[8] solution gives two lines, one strong (3311 cm^{-1}) and the other weak (3394 cm^{-1}). When formalin solution and ammonia are mixed together in the right proportion, heat evolution takes place and hexamine is formed. This is well shown by Raman spectra, since the lines due to hexamine appear in the mixture, but none due to the components.

The present investigation therefore shows that in aqueous solution the crystal lines undergo appreciable changes attributable in general to the influence of the surrounding molecules of water, and especially to hydrate formation.

The author's thanks are due to Sir C. V. Raman, F.R.S., for his kind interest in this work.

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